





Original document



# PROCESS FOR PRODUCING HIGH-STRENGTH SEAMLESS STEEL PIPES EXCELLENT IN SULFIDE STRESS CORROSION CRACKING RESISTANCE

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Abstract of corresponding document: **EP0224591**

A process for producing seamless steel pipes to be used as oil well pipes, line pipes, piping for chemical plants, etc. having both high strength and high sulfide stress corrosion cracking resistance by using inexpensive components, which process comprises increasing the content of C and minimizing the contents of impurities such as P and S, conducting quenching at a relatively slow rate of 1 to 50 DEG C/s after heat treatment, then tempering in a relatively high temperature range of from 680 DEG C to the Ac1 transformation point. The pipe thus obtained has a yield strength of 75 kgf/mm<sup>2</sup> or more and excellent stress corrosion cracking resistance without causing any quenching crack.

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## Specification

PRODUCTION OF HIGH STRENGTH SEAMLESS  
 STEEL PIPE WITH SUPERIOR RESISTANCE  
 AGAINST SULFIDE STRESS CORROSION CRACKING

## Technical Field

The present invention relates to a method of producing a high strength seamless steel pipe with a superior resistance against sulfide stress corrosion cracking. The steel pipe is favorably used for oil well pipes under souring tendency and extremely deepening well, line pipes for sour gas and sour oil, chemical plant pipe

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lines, etc. The invention discloses development outcomes to effectively avoid dangers of occurrence of sulfide stress corrosion cracks under a high yield strength of at least 75 kgf/mm<sup>2</sup>.

#### Technical Background

Since the sulfide stress corrosion cracking resistance is generally deteriorated with increase in strength, Cr-Mo base steel having a yield strength of around 64 to 74 kgf/mm<sup>2</sup> has been to date considered to be most excellent against the above-mentioned oil well deepening and souring tendency to attain both the properties in combination.

According to Japanese patent application laid-open No. 53-78,917, there has been recently developed a steel having about 75 to 90 kgf/mm<sup>2</sup> aiming at improvement on the sulfide stress corrosion cracking resistance through increasing Cr and Mo and adding a larger amount of V as compared with a conventional

Cr-Mo steel having around 65 kgf/mm<sup>2</sup>. However, such a steel is expensive because it contains large amounts of expensive elements such as Mo and V. Further, since a large amount of V is contained, the steel is likely to develop cracks during hot processing in a continuous casting.

#### Japanese patent application laid-open

Nos. 57-19,322 and 57-19,323 proposed La-added steels excellent in sulfide stress corrosion cracking resistance, but the yield strength of these steels is around 80 kgf/mm<sup>2</sup> at the maximum. Therefore the strength is hardly improved when compared with the conventional steels.

Furthermore, Japanese patent application laid-open No. 57-35,622 discloses a high strength oil well steel in which P and S are reduced. However, although the strength of this steel is considerably improved, the stress corrosion cracking resistance is assured only when H<sub>2</sub>S is contained in a small amount under an alkaline environment.

#### Moreover, Japanese patent application laid-open

Nos. 52-52,114 and 54-119,324 propose steels in which the sulfide stress corrosion cracking resistance is improved through making steel grains finer by performing heating at the average heating rate of 3 to 500°C/s in a range of A<sub>c1</sub> transformation point or higher (Japanese patent application laid-open No. 52-52,114) or rapidly performing cooling at about from 1 to 500°C/s (Japanese patent application laid-open No. 54-119,324) for quenching. However, such processes have limit in attaining both high strength and sulfide stress corrosion cracking resistance in combination.

In practice, the yield strength of the steel disclosed in Japanese patent application laid-open No. 54-119,324 is about 65 kgf/mm<sup>2</sup>, while in the case of the steels disclosed in Japanese patent application laid-open No. 52-52,114, the maximum load stress at which no sulfide stress corrosion crack occurs is only 55 kgf/mm<sup>2</sup> (73% of the yield strength) when the yield strength is 75 kgf/mm<sup>2</sup> and only about 40 kgf/mm<sup>2</sup> (44% of the yield strength) when the yield strength is 90 kgf/mm<sup>2</sup>.

Under such current circumstances, there has been recently increased demand for high strength materials having a yield strength of not less than 75 kgf/mm<sup>2</sup> and an excellent sulfide stress corrosion cracking resistance in combination, and seamless pipes of a Ni base alloy such as Hastelloy, or Inconel have been tried to be used as oil well pipes. However, since such materials are too expensive, use thereof is obliged to be restricted. Therefore, development of inexpensive low alloy steel base materials have been strongly demanded.

#### Disclosure of the Invention

An object of the present invention is to advantageously solve the above-mentioned problems, and to provide a process for advantageously producing a seamless steel pipe which is composed of inexpensive

ingredients suitable for continuous casting without containing a large amount of the above-mentioned expensive elements and which has an excellent sulfide stress corrosion cracking-resistance and a high yield strength of from 75 to 120 kgf/mm<sup>2</sup> in combination.

In order to solve the above-discussed problems, the present inventors have acquired the below-mentioned acknowledgement through repeatedly strenuous researches.

(1) While the sulfide stress corrosion cracks are more likely to occur with increase in strength, the higher an annealing temperature, the more excellent the sulfide stress corrosion cracking resistance in the case of the same level strength.

(2) In order to obtain superior sulfide stress corrosion cracking-resistance in the case of the steels having a yield strength of not less than 75 kgf/mm<sup>2</sup>, it is necessary that the annealing temperature is set at not less than 680°C.

(3) In order to stably obtain a yield strength of not less than 75 kgf/mm<sup>2</sup> when the annealing temperature is set at not less than 680°C, it is necessary that Cr and Mo are not less than 0.8% by weight (hereinafter referred to briefly as and 0.6%, respectively, in the case of a Cr-Mo steel containing more than 0.40% of C.

(4) When P is present at not less than 0.020% or S is present at not less than 0.010% in the steel, excellent sulfide stress corrosion cracking resistance can be obtained even when the annealing temperature is set at not less than 680°C.

(5) As compared with a steel having strength improved by Cr and Mo only as stated in the above item (3), a steel further admixed with at least one of Ti, V and Nb is improved in terms of the sulfide stress corrosion cracking-resistance.

In particular, a sour resistance critical stress ratio reaches 90% or more by adopting a Cr-Mo-Ti-V-Nb system. Here, the sour resistance critical stress ratio is a ratio expressed by percentage between the maximum stress at which no sulfide stress corrosion cracks occur at a souring environment and the yield strength of a material.

(6) However, when Cr-Mo steel containing as much as over 40% of C as intended in the present invention is subjected to a quenching treatment in a form of a long and thick pipe such as an oil well pipe, quench cracks occur when it is merely put into a cooling medium such as water or oil from a heated state as ordinarily done.

Therefore, it is necessary to perform cooling relatively slowly. However, when the cooling rate is too small, no quenching is effectuated and the sulfide stress corrosion cracking-resistance after the annealing is remarkably deteriorated.

In order to prevent this, it is necessary that 90% or more of the structure after the quenching are converted

to martensite. For attaining this, it is necessary that the average cooling rate is set at not less than 10°C/s in a range from the heating temperature to around 3000°C at which the martensite transformation is almost completed. On the other hand, in order to prevent the quenching cracks, it is necessary to set the average cooling rate at not more than 500°C/s.

The present invention is based on the abovementioned acknowledgement.

That is, the present invention relates to a process for manufacturing a high strength seamless steel pipe having an excellent sulfide stress corrosion cracking-resistance, which process comprises hot processing hollow raw material for the seamless steel pipe, heating the hot processed raw material up to a temperature of not less than an Ac3 transformation point, quenching the resultant while cooling at the average cooling rate of from 1 to 500°C/s is done in a range from the Ac3 transformation point to at least 3000°C, thereby making conversion into martensite structure, and then annealing a quenched article in a temperature range of from not less than 6800°C to not more than the Ac3 transformation point, said raw material containing: from more than 0.40 to 0.60% of C, from 0.20 to 0.35% of Si, from 0.4 to 1.2% of Mn, from 0.8 to 1.5% of Cr, from 0.6 to 1.0% of Mo, and from 0.005 to 0.1% of Al together with P and S being restricted to not more than 0.020% and not more than 0.010%, respectively, and occasionally further at least one kind of V and Nb in a range of not more than 0.1%.

In the following, the present invention will be concretely explained.

First, the reasons why the components of the raw material are restricted to the respective above ranges according to the present invention will be explained below.

**C : more than 0.40 to 0.60%**

C is an element useful for obtaining a high strength in quenching even at high temperatures.

In particular, in order to stably obtain a yield strength of not less than 75 kgf/mm<sup>2</sup> through annealing at high temperatures of not less than 6800°C as intended by the present invention, at least more than 0.40% C is necessary. If it exceeds 0.60%, there is possibility that quenching cracks occur. Thus, C is added in a range from more than 0.40 to 0.60%.

**Si : 0.20 to 0.35%**

At least 0.20% of Si is necessary to improve deoxidation and strength of the steel. If it exceeds 0.35%, toughness is deteriorated. Thus, Si is restricted to a range from 0.20 to 0.35%.

**Mn : 0.4 to 1.2%**

Mn is an element useful for improving hardenability and strength as well as for deoxidizing.

If the content is less than 0.4%, effect obtained by the addition is poor, while if it exceeds 1.2%, it causes segregation of P, S, etc. to deteriorate the sulfide stress corrosion cracking-resistance. Thus, Mn is included in a range from 0.4 to 1.2%.

**Cr : 0.8 to 1.5%**

Cr forms carbides during quenching and annealing treatment to effectively contribute to increase strength and annealing resistance. For this purpose, it is necessary that 0.8% or more of Cr is added.

If it is added in an amount of more than 1.5%, its effect is not only saturated, but also the sulfide stress corrosion cracking-resistance is inversely deteriorated. Thus, Cr is restricted to a range from 0.8 to 1.5%.

**Mo : 0.6 to 1.0%**

As in the case of Cr, Mo increases strength and resistance against annealing and further effectively contributes to the improvement of the sulfide stress corrosion cracking-resistance through preventing the segregation of P in grain boundaries. If the content is less than 0.6%, effect obtained through the addition is poor. On the other hand, even if it is included at more than 1.0%, its effect is not only saturated, but also toughness tends to be inversely deteriorated and cost rises. Thus, Mo is restricted to a range from 0.6 to 1.0%.

Al : 0.005 to 0.1%

Al is a useful element which not only contributes to deoxidation but also improves toughness, strength and sulfide stress corrosion cracking-resistance through making crystal grains fine upon reaction with N.

However, if the content is less than 0.005%, the effect obtained through the addition is poor, while if it is over 0.1%, the effect is not only saturated, but also the toughness is inversely deteriorated. Thus, the content is restricted to 0.005 to 0.1%.

P : not more than 0.20%; S : not more than 0.010%

Both P and S are harmful elements which cause conspicuous deterioration of the sulfide stress corrosion cracking-resistance of the steel. In order to maintain the intended strength and sulfide stress corrosion cracking-resistance when Mo is added and the annealing temperature is set at a high temperature of 680°C or more according to the present invention, it is necessary that P and S are restrained to not more than 0.020% and not more than 0.010%, respectively.

A molten steel formulated in the above-mentioned preferable ingredient composition is cast, and converted to a hollow material through piercing according to a conventional way.

The thus obtained hollow material for a seamless steel pipe is hot rolled, and then quenched and annealed.

It is necessary to convert 90% or more of the steel structure to martensite structure during the quenching without causing quenching cracks. For attaining this, it is necessary that after the steel is heated at a temperature of not less than  $A_{c3}$  transformation point, it is cooled at the average cooling rate of from 1 to 500°C/s, preferably from 5 to 300°C in a range from the  $A_{c3}$  transformation point to at least 300°C.

The reason why the average cooling rate is restricted to the range from 1 to 500°C/s is that if the average cooling rate is slower than 1°C/s, the steel is not sufficiently quenched and therefore satisfactory sulfide stress corrosion cracking-resistance after the annealing cannot be obtained, while if it exceeds 500°C/s, there is a great possibility that quenching cracks occur.

As a cooling way, various methods are available, for instance, a method of applying a cooling medium to the steel pipe through spraying, showering, fogging, or the like while an amount of the cooling medium, the application pressure, etc. are controlled, a method of cooling the steel pipe with water or oil after the heating in the state that the pipe is preliminarily wrapped with an excellent thermal resistant and excellent temperature-maintaining refractory material prior to the heating, or a method of formulating such a cooling medium as to meet the intended cooling capability.

Any method may be adapted so long as the average cooling rate in the above range is satisfied.

It is necessary to perform annealing treatment at a temperature range of not less than 680°C but not more than the  $A_{c1}$  transformation point. For, in order to obtain the yield strength of from 75 to 120 kgf/mm<sup>2</sup> and the excellent sulfide stress corrosion cracking-resistance as intended by the present invention, it is indispensable to perform the annealing treatment at a high temperature of not less than 680°C. On the other hand, if the temperature exceeds the  $A_{c1}$  transformation point, austenite is produced. Consequently

when the cooling is carried out down to ordinary temperature, the austenite is transformed to the martensite which does not undergo the annealing. Thus, the sulfide stress corrosion cracking-resistance is conspicuously deteriorated.

As mentioned above, the high strength seamless steel pipe having excellent sulfide stress corrosion cracking-resistance can be obtained. According to the present invention, in order to further enhance the strength and the souring critical stress ratio, Ti, Nb and V may be added.

Ti, Nb and/or V : not more than 0.1%

Ti, Nb and V all form carbides as in the case with Cr and Mo during the quenching and annealing treatment, and effectively contribute to the enhancement of the quenchability and resistance against the annealing softening. However, if the addition amount exceeds 0.1%, the precipitates not only become coarse, but also the sulfide stress corrosion cracking-resistance is inversely deteriorated and further the processability and toughness become lowered. Thus, it is necessary that Ti, Nb and V be added in a range of not more than 0.16 either when singly added or when added in combination.

Although the reason why not only the strength but also the sulfide stress corrosion cracking-resistance is remarkably improved when the conditions according to the present invention are met is not definitely clear, it is thought as follows:

That is, the sulfide stress corrosion cracks are thought to be a kind of hydrogen brittleness in which hydrogen generated by the corrosion of the steel with an aqueous solution containing hydrogen sulfide penetrates into the steel and gathers at stress-concentrating locations of the inclusions, precipitates, transformations etc. to embrittle the steel. The stress-concentrating locations at which hydrogen gathers are thought to be conspicuously reduced by reducing P and

S, decreasing the inclusions, decreasing transformation density and making the precipitates spherical through annealing at high temperatures of not less than 680°C, and obtaining structure in which the precipitates are finely and uniformly distributed through annealing at high temperatures after not less than 90% is converted to martensite.

Ordinarily, when the annealing is carried out at high temperatures to attain the above-mentioned low transformation density and spherical precipitates, the strength of the steel becomes lower. According to the ingredient combination of the present invention, however, it is considered that the tissues having the precipitates with appropriate profile and distribution can be obtained so that the high strength can be obtained without deteriorating the sulfide stress corrosion cracking-resistance.

#### Best Mode for Carrying out the Present Invention

A seamless steel pipe hollow material having an ingredient composition shown in Table 1 was hot processed, heated up to the Ac<sub>3</sub> transformation point, cooled at the average cooling rate shown in Table 1 and then subjected to an annealing treatment at a temperature given in Table 1, thereby obtaining a product.

The yield strength (Y.S.), the tensile strength (T.S.) and the sulfide stress corrosion cracking resistance of the thus obtained seamless steel pipes were examined, and results thereof are shown together in Table 1.

The sulfide stress corrosion cracking-resistance was evaluated by a test in which a stress being 80% of the yield strength was loaded while a round bar tensile test piece was immersed into an NACE liquid (0.5% acetic acid, and saturated hydrogen sulfide aqueous solution containing 5% of sodium chloride). "o" mark and "x" mark show non-broken samples and broken samples in the test for 30 days, respectively.

Table 1(1)-a  
EMI14.1

<tb> <SEP> Chemical <SEP> ingredient <SEP> (% <SEP> by <SEP> weight)  
 <tb> No. <SEP> Kind  
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Table 1(1)-b

EMI15.1

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EMI16.1

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 corrosion <SEP> Quenching  
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 <tb> Table 1(2)-b

EMI17.1



<SEP> Average <SEP> Sulfide  
 <tb> <SEP> cooling <SEP> Annealing <SEP> stress  
 <tb> No.<SEP> Kind <SEP> rate <SEP> during <SEP> temperature <SEP> YS <SEP> TS <SEP>  
 corrosion <SEP> Quenching  
 <tb> <SEP> quenching <SEP> ( C) <SEP> (kgf/mm) <SEP> (kgf/mm) <SEP> cracking- <SEP> crack  
 <tb> <SEP> ( C) <SEP> resistance  
 <tb> 14 <SEP> Comparative <SEP> 20 <SEP> 700 <SEP> 87 <SEP> 106 <SEP> x <SEP> not  
 <tb> <SEP> steel <SEP> occurred  
 <tb> 15 <SEP> " <SEP> 30 <SEP> 690 <SEP> 88 <SEP> 107 <SEP> x <SEP> "  
 <tb> 16 <SEP> " <SEP> 20 <SEP> 700 <SEP> 96 <SEP> 116 <SEP> x <SEP> "  
 <tb> 17 <SEP> " <SEP> 30 <SEP> 690 <SEP> 82 <SEP> 100 <SEP> x <SEP> "  
 <tb> 18 <SEP> " <SEP> 40 <SEP> 700 <SEP> 70 <SEP> 85 <SEP> o <SEP> "  
 <tb> 19 <SEP> " <SEP> 20 <SEP> 705 <SEP> 88 <SEP> 106 <SEP> x <SEP> "  
 <tb> 20 <SEP> " <SEP> 10 <SEP> 705 <SEP> 90 <SEP> 109 <SEP> x <SEP> "  
 <tb> 21 <SEP> " <SEP> 20 <SEP> 705 <SEP> 79 <SEP> 92 <SEP> x <SEP> "  
 <tb> 22 <SEP> " <SEP> 20 <SEP> 705 <SEP> 82 <SEP> 93 <SEP> x <SEP> "  
 <tb> 23 <SEP> " <SEP> 10 <SEP> 705 <SEP> 83 <SEP> 94 <SEP> x <SEP> "  
 <tb> 24 <SEP> " <SEP> 60 <SEP> 685 <SEP> 90 <SEP> 110 <SEP> o <SEP> occurred  
 <tb> 25 <SEP> " <SEP> 0.8 <SEP> 685 <SEP> 80 <SEP> 102 <SEP> x <SEP> "  
 <tb> 26 <SEP> " <SEP> 50 <SEP> 680 <SEP> 63 <SEP> 73 <SEP> o <SEP> "  
 <tb> 27 <SEP> " <SEP> 40 <SEP> 700 <SEP> 65 <SEP> 76 <SEP> o <SEP> "  
 <tb>

As obvious from the Table, all the seamless steel pipes (Nos. 1-10) obtained according to the present invention exhibit high YS and TS values as well as excellent sulfide stress corrosion cracking-resistance

To the contrary, Comparative steels (Nos. 11 and 12) in which the ingredient composition satisfied the appropriate ranges but the annealing temperature did not reach the lower limit and Comparative steel (N 25) in which the cooling rate during quenching did not reach the lower limit were poor in the sulfide stress corrosion cracking-resistance. Comparative

Steel (No. 24) of which the cooling rate during quenching exceeds the upper limit was excellent in the sulfide stress corrosion cracking-resistance, but produced the quenching cracks.

Among the steels (Nos. 13-23, 26, and 27) in which any of the ingredients falls outside of the appropriate range of the present invention, Steels (Nos. 18, 26 and 27) in which C-content was less than the lower limit were good in the sulfide stress corrosion cracking-resistance, but gave only the lower YS and TS values. The other steels (Nos. 13-17) and 19-23) were excellent in the YS and TS values, but were poor in the sulfide stress corrosion cracking-resistance.

#### Industrial applicability

According to the present invention, it is possible to obtain the seamless steel pipe which is composed of inexpensive ingredient system containing no great amount of expensive elements unlike the prior art and suitable for the continuous casting and which has the high strength of the yield strength of from 75 to 12 kgf/mm<sup>2</sup> and is free from the development of the sulfide stress corrosion cracks under the load stress of 80% of the yielding stress. Thus, the present invention is advantageously suited particularly for the oil and gas pipes and line pipes for souring gas and souring oil under the tendency that the wells become deeper under the stronger souring and further pipe lines for the chemical plant.

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Claims of corresponding document: **EP0224591**

What is claimed is:

1. A method of manufacturing a high strength seamless steel pipe being excellent in sulfide stress corrosion cracking-resistance, which comprises hot processing a hollow raw material for the seamless steel pipe containing from over 0.40 to 0.60 wt% of C, from 0.20 to 0.35 wt% of Si, from 0.4 to 1.2wt of Mn, from 0.8 to 1.5 wt% of Cr, from 0.6to 1.0 wt% of Mo, from 0.005 to 0.1 wt% of Al with P being restrained to not more than 0.020 wt% and S being restricted to not more than 0.010 wt%, performing heating at a temperature not lower than Ac3 transformation point, and effecting quenching in which cooling is done the average cooling rate 1 to 500C/s from said temperature to at least 3000C to produce a martensite tissues, and then effecting annealing in a temperature range of not lower than 6800C and not higher than Ac1 transformation point.

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